Message

From: Paul Resnick [Ex. 6 Personal Privacy (PP)]
Sent: 2/8/2019 4:21:21 PM
To: Strynar, Mark [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=5a9910d5b38e471497bd875fd329a20a-Strynar, Mark]
Subject: Decomposition of MS Samples in the MS

Mark,

Given the harsh conditions [heat, water present] in the MS to which the samples are exposed and the finite stability of the chemicals in the river water samples it is possible that the fluorinated compounds in these samples may partially be converted to other compounds. Yes, the time the sample is exposed to these conditions is low but the hypothesis should be tested experimentally.

1. I would expect some $CHF(COOH)_2$ to decarboxylate under the MS conditions. If so the product could be CH_2FCOOH mw = 78. Is there a 78 peak that was found in the river water samples. ***The absence of malonate means nothing since I expect its formation and river discharge would not be continuous but rather occur only at times when there was an upset in the process operation and which may not have been occurring when the river water samples were obtained.***

2. A good experiment would be to inject a known sample of $HOOCCF(CF_3)OCF_2CF(CF_3)OCF_2CF_2SO_3H$ and look for it in the MS along with the two possible decomposition products $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_3H$ and $CF_3CFHOCF_2CF(CF_3)OCF_2CF_2SO_3H$. The last two structures are well known to you as Nafion 1 and 2. All the compounds have been written as the free acid but you will deal with them as the anions.

3. The precursor to the carboxylate monomer is $HOOCCF(CF_3)OCF_2CF(CF_3)OCF_2CF_2COOH$. The thermal stability due to loss of CO_2 is greater for OCF_2CF_2COOH than for $HOOCCF(CF_3)O$ so that one can not rule out that the source of $CF_3CFHOCF_2CF(CF_3)OCF_2CF_2COOH$ could be the decomposition of the carboxylate monomer precursor during the MS analysis. Or perhaps a portion of it.

4. There should not be a problem with Gen-X if the conditions in the MS are the same as when you use standards of Gen-X. The analogous decarboxylation will give $CF_3CF_2CF_2OCFHCF_3$ i.e. E-1 which will not be seen in the MS analysis. But, since the same percentage of Gen-X may be decarboxylated in the samples and standard the concentrations reported would be correct.

5. PFOS is much more thermally stable that PFOA i.e. $-CF_2SO_3H$ is more stable than $-CF_2COOH$. The SO_3H group should survive the MS conditions. Thus the results of experiment 2 above should go a long way to show if Nafion 1 and Nafion

2 are indeed in the river or are derived in all or in part from the Nafion monomer precursor. Most likely they may arise from the decarboxylation of the precursor in the sample as well as being present in the starting river water sample. When you get standards of Nafion 1 and Nafion 2 you should be able to tell where they came from. By analogy you should be able to estimate the amount of Gen-X that decomposes in the MS.

Should we discuss this?

Paul

A) The rate of decarboxylation (loss of CO_2) in water at 150° is 1400 times faster for $CF_3CF_2CF_2OCF(CF_3)COOK$ than CF_3CF_2COOK.
B) From US 8329813 (2012) to DuPont:

TABLE 1

Compound	Linear/ Branched	Temp/C. Complete Wt Loss*	Temp/C. Max Decarboxylation**	$t_{1/2\ (min)}$ at 200° C. in air***
$C_3F_7OCF(CF_3)CO_2NH_4$	Branched	197	207	~5
$C_2F_5OCF(CF_3)CO_2NH_4$	Branched	189	178	~10
$C_2F_5O(CF_2)_3CO_2NH_4$	Linear	180	240	~90
$C_2F_5O(CF_2)_5CO_2NH_4$	Linear	179	240	
$C_3F_7O(CF_2)_2CO_2NH_4$	Linear	190	247	~90
$C_3F_7O(CF_2)_3CO_2NH_4$	Linear	180	240	
$C_3F_7O(CF_2)_5CO_2NH_4$	Linear	181	240	

*temp at which all samples were either evaporated or decomposed (decarboxylated).
**temp at which maximum amount of CO2 was observed during the TGA experiments.
***half life of surfactants to undergo decarboxylation at 200 C in air.

Note the difference between the branched COOH including Gen-X and the straight chain COOH in thermal stability.

From: Strynar, Mark
Sent: Monday, February 04, 2019 9:44 AM
To: Paul Resnick
Subject: a few things

Paul,

I have looked and been unsuccessful in finding fluoromalonate in any sample based on what I expect. My next step is to get a standard and see what MS form it takes when I do have it in the system.

The second thing is I recall discussing with you at some point what you thought was the precursor source for the PFPeA (C5) we find in the water in Fayetteville. This is the chemical CF3 (CF2)3 COOH. I recall writing down suspect source in some notes I took but can't recall what it I had noted. I expect some acyl fluoride produced as a side product of one of the vinyl ethers made in Fayetteville.

Mark

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